INVESTIGATING THE USE OF BIOSORBENTS TO REMOVE ARSENIC FROM WATER

A Thesis

by

SHREYAS ANAND ERAPALLI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2010

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bryan Boulanger
Committee Members,	R. Autenrieth
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Head of Department,	John Niedzwecki

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ABSTRACT

Investigating the Use of Biosorbents to Remove Arsenic from Water.

(December 2010)

Shreyas Anand Erapalli, B.Tech, National Institute of Technology Karnataka Surathkal

Chair of Advisory Committee: Dr. Bryan Boulanger

Evaluating the ability of biosorbents to remove arsenic from water has global significance due to the widespread availability and low cost of biosorbent materials. In this study, the ability of coffee grounds and coconut substrate (two previously unreported biosorbents) to remove arsenic from water was compared against the performance of arsenic removal on rice husk (a recognized and widely tested biosorbent). The three biosorbents were individually screened for their ability to remove arsenite, As (III), and arsenate, As (V), from water.

Batch reactors were employed to assess the percent removal, reaction kinetics, adsorption capacity, and desorption of each arsenic species onto/from biosorbents under pH buffered and non-buffered conditions. The resulting experimental data was statistically interpreted using analysis of variance and t-testing of the means. The experimental results were also fit to existing kinetic and isotherm models to provide kinetic rate constants, the maximum adsorption capacity, and to help interpret the nature of the reactions on the biosorbent surface.

While all three biosorbents removed arsenic with similar initial reaction kinetics (pseudo 1st order reaction rate constant for As (III) was 0.13 hr^{-1} for all three biosorbents and for As (V) was 0.17 hr^{-1} for coffee grounds and rice husk and 0.15 hr^{-1} for coconut substrate), the amount of arsenite and arsenate removed was highest for coffee grounds (84 and 91%, respectively), followed by rice husk (68 and 72%, respectively), and then coconut substrate (26 and 24%, respectively). The maximum adsorption capacity of arsenite and arsenate was determined for coffee grounds (0.66 and 0.70 mg/g, respectively) and rice husk (0.55 and 0.66 mg/g, respectively). While desorption was observed for both coffee grounds and rice husk, the total amount of desorption accounted for less than 15% of the total retained mass. The results of this thesis work reveal that coffee can be used as an effective biosorbent when compared to rice husk; however, coconut substrate is less effective than rice husk at removing As (III) and As (V).

DEDICATION

This work is dedicated to my family.

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I would most of all like to express my deep gratitude to Dr. Bryan Boulanger, my advisor, for his guidance and supervision not just throughout my research project but also otherwise. He has always been there to support me with his friendly nature in various ways whenever I have needed him. I have come to respect him for his humanitarian attitude and admire the many hats that he wears splendidly at all times.

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NOMENCLATURE

AAS	Atomic Adsorption Spectrometer
As (III), $NaAsO_2$	Sodium Arsenite
As (V), As_2O_5	Arsenic Pentoxide
SEM	Scanning Electron Microscopy
NaOH	Sodium Hydroxide
ANOVA	Analysis of Variance
ICPMS	Inductively Coupled Plasma Mass Spectrometry
μg	Micrograms
ppb	Parts per Billion
XPS	X-Ray Photoelectron Spectroscopy
$NaBH_4$	Sodium Borohydride

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1. INTRODUCTION

Arsenic is a colorless and odorless Group V element discovered in 1250 AD. Arsenic has an atomic number of 33 and is the 20th most abundant element that primarily occurs as an oxide [1-2]. In its inorganic form, arsenic is a gray colored metalloid. Arsenic is insoluble in its native state, but combines with other elements to form soluble compounds. Arsenic has an atomic weight of 74.9, a specific gravity of 5.73 [1], and is a hazardous and toxic chemical to humans and animals even at small dosages [3].

1.1. Occurrence of Arsenic in Natural Systems

Arsenic is present throughout the earth's crust and is present in air, water, and soil in trace quantities [4-5]. In the atmosphere arsenic is found due to release of volcanic ash, industrial processing releases, and weathering of rocks. Industrial processes releasing arsenic to air include burning of coal, smelting of ores, and use of pesticides [5-6]. Volatilization of arsenic from soil also contributes to arsenic concentrations in air in the form of organic arsines [7]. High levels of arsenic are also found in fish. The amounts of arsenic in fish are quite high when compared to other environmental media. However, arsenic in fish is largely organic and as a result it is non toxic [4].

Soil concentrations of arsenic vary greatly by region and are normally a function of mineral weathering. Pesticides, defoliants and herbicides also contribute to the arsenic content in soil [7]. Arsenic is introduced into surface and groundwater through point source and non-point source pollution and from natural deposits. In environmental waters, arsenic is present

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This thesis follows the style of Journal of Hazardous Materials.

predominantly as either arsenate (as As (V)) or arsenite (as As (III)) based upon the redox conditions of the system. However, arsenic rarely occurs in an uncomplexed state [8]. Because arsenic is a common ground and surface water contaminant, arsenic is also a common occurring drinking water contaminant that is difficult to completely remove from drinking water sources with existing water treatment technologies [9-10].

Arsenic contamination of groundwater and surface waters used as drinking water sources occurs both naturally (groundwater contact with mineral deposits) or from human activities (surface water contamination with fertilizers and pesticides and industrial discharge) all around the world [11-12]. Thermal springs of New Zealand, Japan and Alaska have been reported to contain arsenic concentrations above 10 μg/L from natural causes [13]. Industrial discharge adds arsenic contamination of environmental waters above naturally occurring contamination. Industrial activities such as smelting of copper and other non ferrous materials, and burning coal and fossil fuels releases arsenic into surface water systems [4, 10].

1.2. Arsenic Contamination of Drinking Water: A Global Perspective

In Bangladesh, India, Mexico, Chile, Argentina, Nepal and a few other parts of the world, arsenic contamination of drinking water supplies is a major public health emergency. Arsenic concentrations in drinking water in these countries have been found to exceed 1000 ppb (mainly from contaminated well water) [14]. Nowhere is the problem worse than in Bangladesh where an estimated 80% of the country's total groundwater reserve is believed to be affected by naturally occurring arsenic contamination in groundwater due to oxidation of

arsenopyrite [15-16]. 40 million people are at risk of arsenicosis in Bangladesh alone [17].

Although arsenic concentrations in US water supplies are not as high in other parts of the world, many groundwater wells in States such as New Mexico, Arizona, Texas and California contain arsenic above 50 ppb [14]. Historical monitoring of major groundwater and surface source waters in the Rio Grande Valley in Texas exhibit variable levels of arsenic at high enough levels to cause concern [18]. Arsenic concentrations above the Texas State Screening level of 5 μg/L and the Federal criteria of 10 μg/L for both surface and groundwater are common in drinking water throughout the Rio Grande Valley, with the highest reported total arsenic concentrations of 33 μg/L for surface waters in the Rio Grande and 569 μg/L in groundwater sampled from the Jasper Aquifer in Duval County [19]. Private water wells in rural South Texas are known to contain arsenic and many of these wells have been shutdown or require immediate treatment. Table 1 reports a summary of arsenic concentrations measured in groundwater from around the world. The concentrations range from a few ppb to few thousands of ppb in the water.

Table 1

Arsenic in groundwater around the world [14].

Country or Area	Population at risk	Groundwater Concentration (μg As/l)	Guidelines (μg As/l)	Discovery Date
Argentina	2,000,000	100-1000	50	1981
Bangladesh	50,000,000	<1-4700	50	1980s
Bolivia	20,000		50	1997
Chile	437,000	900-1040	50	1971
China, Inner Mongolia	600,000	1-2400	50	1990s
China, Xinjiang Province	100,000	1-8000	50	1980s
Hungary	220,000	10-176	10	1974
India, West Bengal	1,000,000	<10-3900	50	1980s
Mexico	400,000	10-4100	50	1983
Nepal	Unknown	Up to 456	50	2002
Peru	250,000	600	50	1984
Romania	36,000	10-176	10	2001
Taiwan	200,000	10-1820	10	1950s
Thailand, Ronpibool	1,000	1-5000	50	1980s
USA	Unknown	10-48000	10	1988
Vietnam	1,000,000+	1-3050	10	2001

1.3. Health Effects of Arsenic Exposure

The current World Health Organization recommended guideline for arsenic in drinking water is 10 μg/L. However, drinking water in many developing countries contains arsenic concentrations above 50 μg/L due to lack of

sufficient implementation of removal technologies in these countries [20]. Arsenic is a carcinogen and exposure to arsenic from drinking water can lead to acute and/or chronic disease in humans. Acute exposure results in abdominal pain, bloody diarrhea, and vomiting. Arsenic exposures can also lead to cardiovascular problems, such as shock and hypotension and can affect the central nervous system[21-22].

Long-term arsenic exposure results in various diseases that differ between geographical areas and population groups. Chronic exposure leads to carcinogenic and/or non-carcinogenic effects. Non-carcinogenic effects include skin irritation, pigmentation, skin lesions, hyperkeratosis, liver damage, and kidney damage. Studies have shown that women who were exposed to arsenic at work or had arsenic exposure near their homes, had higher miscarriage rates and their children have been found to have lower average weight at birth compared to non-exposed control populations [23].

Arsenic produces a carcinogenic effect through inhalation, ingestion and dermal contact. The carcinogenic diseases caused by chronic exposure include skin, lung, and liver cancer [23-24]. Chronic exposures are the highest cause for concern as they can occur at low dosages over long and often undetected exposure durations [25]. Studies on human populations in Taiwan and Chile have concluded that a 50 ppb arsenic concentration in drinking water is estimated to cause a cancer mortality of 1 in 100 [26].

1.4. Arsenic Chemistry in Drinking Water Sources

Figure 1 shows the oxidation-reduction potential (E_h) of arsenic as a function of pH. E_h measures the reducing potential (ability to accept electrons) of a given

chemical species. In drinking water sources arsenic is present in the As (V) oxidation state as the (AsO_4^{-3}) anion under aerobic conditions and in the As (III) oxidation state under reducing conditions as $As(OH)_3$ [27].

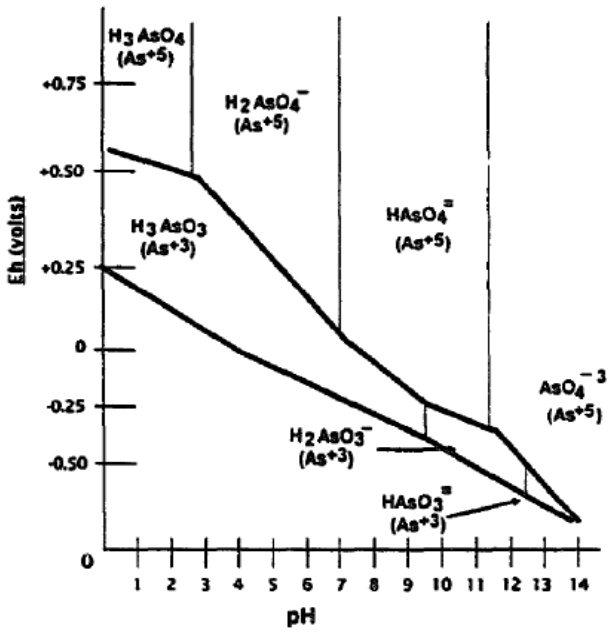


Figure 1. Speciation of arsenic in water adapted from [27].

As seen in Figure 1, pH also plays an important role in determining the ionic state of the arsenic in drinking water sources. As (III) and As (V) ionic speciation as a function of pKa can be expressed by the following equations:

As (III)

$H_3AsO_3 \rightarrow H^+ + H_2AsO_3^-$ pKa = 9.22

$H_2AsO_3^- \rightarrow H^+ + HAsO_3^-$ pKa = 12.3

As (V)

$H_3As0_4 \rightarrow H^+ + H_2As0_4^-$ pKa = 2.2

$H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-}$ pKa = 7.08

$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$ pKa = 11.5

where the dissociation constant (pKa) is an equilibrium constant and logarithmic measure of the strength of an acid in solution. The combined pH and Eh conditions of the system will determine the form of arsenic found in water.

Other reactions that also occur with arsenic species in an aquatic environment include ligand exchange, occlusion, and precipitation [28]. Arsenic solubility is also affected by the presence of iron with the most stable arsenate complex formed on combination with Fe(II) [28].

1.5. Treatment Technologies Used to Remove Arsenic from Drinking Water Sources

Developing technologies to remove arsenic from drinking water has become a major topic of research in recent years. As (III) is more difficult to remove, because arsenite occurs as a non-ionized compound under most environmental pH ranges. A strong oxidant, such as free chlorine or permanganate is required to oxidize arsenite to arsenate, which exists as an anion under normal

pH environmental conditions. The arsenate anion is easier to remove due to its ionic state [29].

Most removal technologies that currently exist for arsenic strive to achieve maximum arsenic removal for minimalistic associated costs for use in centralized water purification systems [30]. The most effective technologies used to remove arsenic from drinking water sources rely upon membrane separation, lime softening, coagulation, electrodialysis, and sorption [31-32]. Table 2 represents the most suitable removal technologies identified by the US Environmental Protection Agency [33].

Table 2

Efficacy of arsenic removal by technology adapted from [33].

Treatment Technology	**Maximum Removal (%)**
Membrane Separation	>95
Modified Lime Softening (pH > 10.5)	90
Modified Coagulation/Filtration	95
Electrodialysis Reversal	85
Adsorption	95

A brief description of each technology presented in Table 2 follows:

1.5.1. Membrane Separation

Membrane based separation technologies, such as ultrafiltration, microfiltration, nanofiltration, charged filtration, cross flow microfiltration, magnetic filtration, and reverse osmosis successfully remove arsenic from contaminated water[34]. Membrane filtration (ultrafiltration, microfiltration, and reverse osmosis) separates particles on the basis of size exclusion to remove colloidal particles across a membrane with a pressure gradient. It is desirable to achieve maximum separation at lowest fouling possible[34]. In the case of charged filtration, the membrane used has a negative charge that reduces fouling of the membrane and increases the membranes operational lifetime. Cross flow microfiltration utilizes a moving membrane to attempt to reduce fouling using a nebulizer [35].

1.5.2. Lime Softening

The addition of lime (calcium hydroxide) is an effective process for removing arsenic from water most often used in centralized treatment systems (see Figure 2). However, lime softening shifts the pH to alkaline conditions (pH > 10.5) causing calcium and magnesium carbonate precipitates that also entraps and removes arsenic. Lime softening is also significantly enhanced in the presence of chlorine, but the softened water requires acid neutralization prior to distribution [36].

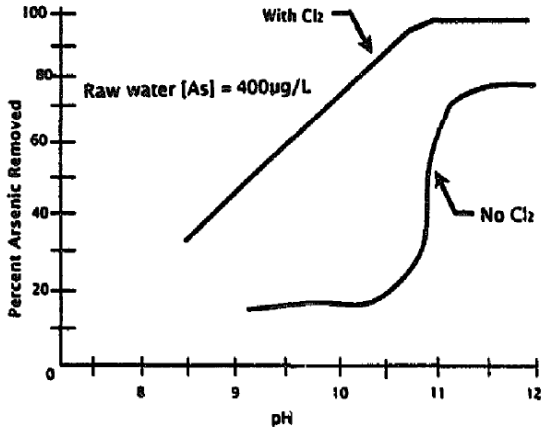


Figure 2. Arsenic removal by lime softening as a function of pH adapted from [36] .

1.5.3. Coagulation

Coagulants such as ferric chloride and alum (hydrated potassium aluminum sulfate) have demonstrated arsenic removal in both centralized treatment and point-of-use treatment systems. Coagulation is also accompanied by disinfection, generally, using chlorine. The primary mechanism of arsenic removal during coagulation is entrapment followed by sedimentation. In some cases where arsenic is soluble the surface interactions of the alum flocs with the arsenic enable removal through coagulation. Studies have shown that As (V) is far easier to remove by this method compared to As (III) because As (V) exists as a charged species at environmental pH levels whereas As (III) exists as a neutral species. However, the addition of chlorine primarily for disinfection also triggers the oxidation of As (III) into As (V), which then can be removed [36]. It is important to note that many of the coagulants act as chemisorbents to remove arsenic [37-39].

1.5.4. Electrodialysis

Electrodialysis is also a membrane water treatment process. However, instead of applying pressure in order to drive water through a membrane, electrodialysis involves using an electric current to attract ions through the membrane to achieve the separation [27] . Arsenic is removed via anions separation, but if As(III) is present an oxidant must be added to oxidize As(III) to As(V) and form anions in solutions [27].

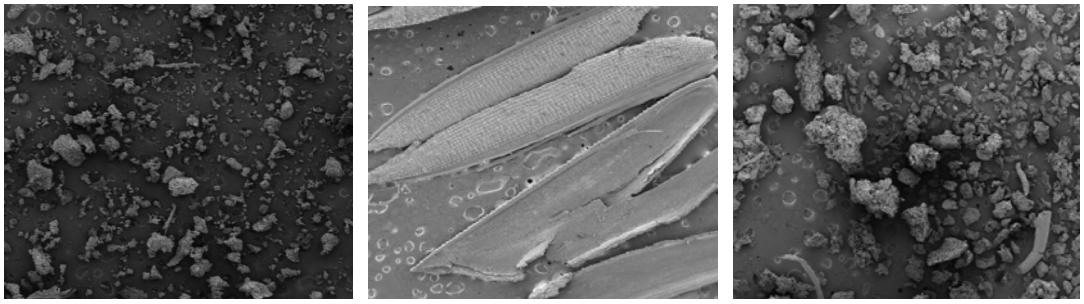
1.5.5. Adsorption

Arsenic removal is also achieved through adsorption on commercial adsorbents, clays, zeolites, ion exchange and chelating resins, and biosorbents. For commercial ion-exchange and chelating systems, arsenic contaminated water flows through the exchange media and the arsenic ions exchange with the surface of the oppositely charge resins. Ion-exchange resins and chelating resins have high efficiency of arsenic removal. Commercial adsorbents including activated carbons and polymeric resins are widely used in arsenic removal. Various forms of activated carbon used in arsenic removal originate from peat sawdust, coconut, fertilizer waste, blast furnace slag, fly ash, petroleum and waste rubber [1]. Metal oxides, clays, zeolites, and biosorbents demonstrate lower adsorption capacity in comparison to their commercial counterparts, but are less expensive.

Arsenic removal by adsorption onto biosorbents is of particular interest globally due their wide availability and extreme low cost. The use of naturally available sorbents, in place of higher cost commercial products, has led to investigations focusing on arsenic removal from water using sawdust, neem bark, rice husk, biochar, various seeds, and straw (as examples) [40]. However,

based on the review of research literature conducted for this study, coffee grounds and coconut substrate have not previously been investigated for their potential to adsorb arsenic from water.

An interest in assessing the ability of these biosorbents to remove arsenic from water stems from their ready availability of these materials in two communities Dr. Boulanger has been working on long-term water development projects. Their low cost nature and ease of availability along with a lack of prior research on their role as a biosorbent is the basis of this thesis. SEM images of the coffee grounds, coconut substrate, and rice husk used in this study are shown in Figure 3. At the same magnification, the rice husk has a thin, continuous structure whereas the coffee grounds and coconut substrate have a discrete structure without any uniform shape or size.



a) Coffee Grounds b) Rice Husk c) Coconut Substrate

Figure 3. SEM images of biosorbents showing microstructure of their respective surfaces evaluated in this study.

2. RESEARCH HYPOTHESIS AND OBJECTIVES

The hypothesis of this research is that coffee grounds and coconut substrate serve as biosorbents to remove arsenic from water. This hypothesis will be tested against arsenic removal on rice husk which is a recognized biosorbent for arsenic. The three main objectives serving to test this hypothesis are listed along with the specific aims carried out under each hypothesis in the following text.

Objective 1: Evaluate arsenic removal kinetics on coffee grounds and coconut substrate in buffered and non-buffered pH conditions

- Aim 1: Develop laboratory techniques to use different biosorbents for As (V) and As (III) removal from water.
- Aim 2: Run kinetic experiments to investigate the rate and extent of arsenic adsorption on coffee grounds and coconut substrate.
- Aim 3: Identify the reaction order that best describes the removal of arsenic species on coffee grounds and coconut substrate.
- Aim 4: Compare arsenic removal kinetic rate constants for coffee grounds and coconut substrate against the arsenic removal kinetic constant for rice husk

Objective 2. Determine the adsorption capacity of the biosorbents for arsenic removal under buffered and non-buffered pH conditions

Aim 1: Run isotherm studies to determine the adsorption capacity for the biosorbents for As (V) and As (III).

Aim 2: Model experimental results against common isotherm models to determine the maximum adsorption capacity for each investigated biosorbent and to help elucidate the nature of the biosorbent surfaces.

Aim 3: Compare arsenic adsorption capacity of the biosorbents.

Objective 3. Evaluate the desorption of arsenic from the biosorbents under buffered and non-buffered pH conditions

Aim 1: Evaluate desorption of As (V) and As (III) from the biosorbents.

3. EXPERIMENTAL METHODS

3.1. Materials

The three adsorbents used in this study include finely ground coffee beans, rice husk with chaff, and coconut substrate. Coffee grounds were obtained from Starbucks in College Station at no charge; rice husk were obtained from a provisional grocery store in India at a nominal charge of 50 cents per pound; and coconut substrate was purchased from Petco Inc. in College Station. Arsenite (As III) in the form of $NaAsO_2$ (salt) and arsenate (As V) in the form of As_2O_5, sodium borohydride ($NaBH_4$, 98%), hydrochloric acid (HCl), and sodium hydroxide (NaOH, 97%) were purchased from Sigma-Aldrich (St Louis, USA). A Barnstead nanopure water system generated the de-ionized water (with a resistivity greater than 17.7 MΩ) used throughout these studies. pH buffered solutions were prepared using sodium bicarbonate at a molarity of 10 mM.

3.2. Arsenic Analysis

A Solaar M6 Atomic Absorption spectrometer equipped with a V90 Thermo Elemental Hydride Generator with hydrochloric acid and sodium borohydride eluents was used to determine the concentration of As (III) or As (V) in aqueous reactor samples. The analysis was carried out under an air-acetylene gas flame. The concentration of arsenic in the samples was determined based on the flame method response of the instrument for the sample compared to the instrument response using a five point external calibration curve (calibration standards of 5, 10, 15, 20 and 25 ppb).

3.3. Kinetic Experiments

The reaction kinetic experiments were conducted to establish the order of the reaction that most closely represents and characterizes the experimental data. A total of 12 experiments were carried out to assess the kinetic rate constants for adsorption of arsenate and arsenite onto the biosorbents. For each experiment, 15 mg of a biosorbent was added to 15 ml of buffered or non-buffered solution containing arsenite or arsenate resulting in a biosorbent concentration of 1 g/L and an initial aqueous phase arsenic concentration of 500 ppb in each reactor. Three reactors were used to assess the mean and standard deviation concentration of arsenic in the aqueous phase over eight time intervals over 48 hours (including t= 0,2, 4, 8,16,24,36 and 48 hours). Table 3 summarizes the experiments carried out during the kinetic studies.

Table 3

Kinetics experimental setup.

Arsenic Species	Buffer Conditions	Expt. #	Biosorbent	Number of Reactors
As (III)	Buffered	1	Coffee Grounds	3 replicates X 8 time intervals
		2	Rice Husk	
		3	Coconut Substrate	
	Non Buffered	4	Coffee Grounds	3 replicates X 8 time intervals
		5	Rice Husk	
		6	Coconut Substrate	
As (V)	Buffered	7	Coffee Grounds	3 replicates X 8 time intervals
		8	Rice Husk	
		9	Coconut Substrate	
	Non Buffered	10	Coffee Grounds	3 replicates X 8 time intervals
		11	Rice Husk	
		12	Coconut Substrate	

During the kinetic experiments, reactors were placed on a shaking rotator to completely mix the contents of the reactor. At the end of each time interval, the rotator was stopped, the samples for the specified time interval were removed, and the sorbate and sorbent from the removed sample were transferred to seven microcentrifuge tubes. The tubes were placed in a

microcentrifuge and centrifuged at 14000 rpm for 40 minutes. After centrifugation, the original 15 ml sample was separated out as a supernatant in a separate 15 ml tube and was analyzed for arsenic composition using an atomic absorption spectrometer.

3.3.1. Reaction Order Determination

The order of reaction was determined by modeling the resulting experimental data against common kinetic models. For the experimental reaction system, the sorption of arsenic onto the biosorbents can be represented by the following reaction:

$$As + Biosorbent \leftrightarrow As{\equiv}Biosorbent$$

The overall rate law equation for this reaction with respect to arsenic removal as a function of time is then:

$$d[As]/dt = k_f [As][Biosorbent] - k_r [As{\equiv}Biosorbent]$$

where [As] is the concentration of arsenic in the aqueous phase within reactors, [Biosorbent] is the concentration of the biosorbent in the reactors, [As≡Biosorbent] is the resulting sorbed fraction of arsenic and k_f and k_r are the forward and reverse rate constants of the reaction respectively. However, in order to describe the removal kinetics for this reaction, we initially assume that the reaction only proceeds from left to right ($k_r = 0$) and the overall rate law equation now becomes:

$$d [As]/dt = k_f [As][Biosorbent]$$

and the reaction order becomes second order based upon the reaction constituents [41].

However, for the purpose of this work we assess the experimentally derived data against pseudo first order, pseudo second order, and modified second order reaction models because the biosorbent is supplied in excess (pseudo first order) [42] and we were interested in understanding the effect of the buffer on the kinetics (pseudo second order) [42] . Also, a modified second order equation (Ritchie second order equation with no pre-adsorbed surface coverage [43]) was used to fit the data because we were interested in seeing if we could model the effect of adsorbate as well as the excess biosorbents in the reaction with a unit initial biosorbent loading constant, β (β =1) .

The model that best fit the experimental data was used to determine the rate constant of the reaction. The best fit model was decided by comparing the linear regression (r^2) and the sorption capacity error as a function of time (Δq %) for each model. r^2 is the square of the Pearson product moment correlation coefficient between the predicted sorption capacity of the biosorbent at each time interval and the mass ratio of adsorbate adsorbed to adsorbent for each time period. The error is defined as:

$$\Delta q\ (\%) = 100 \cdot \left(\left(\sum \left[\left(m_{t,experimental} - m_{t,modeled}\right)/m_{t,experimental}\right]^2\right)/(n-1)\right)^{1/2}$$

Where m_t = amount of arsenic adsorbed at any time (g); t = reaction duration (hours); and n = number of data points.

3.4. Isotherm Experiments

Isotherm experiments were conducted to assess the adsorption capacity of the biosorbents. A total of four experiments were used to determine the adsorption capacity of coffee grounds. Isotherms for coconut husks were not

carried out based upon the results of the kinetic experiments. Table 4 provides the experimental outline for the isotherm experiments:

Table 4

Isotherm experimental setup.

Arsenic species	Buffer Conditions	Expt #	Adsorbent	Expt duration (hrs)	Number of reactors
As (III)	Buffered	1	Coffee Grounds	36	3 samples X 5 adsorbate concentrations
		2	Rice Husk	36	
As (V)	Buffered	3	Coffee Grounds	36	
		4	Rice Husk	36	

For each isotherm experiment, 15 mg of biosorbent was added to reactors containing 200, 400, 600, 800 and 1000 ppb arsenic in buffered solution. Triplicate reactors were prepared for all 5 concentrations in order to determine the mean and standard deviation concentration of arsenic in the aqueous phase at equilibrium. The 36 hour duration was selected based upon the time to achieve equilibrium inferred from the results of the kinetic studies.

3.4.1. Isotherm Models

Adsorption isotherms are used to determine the amount of adsorbate (arsenic) that can be adsorbed on the adsorbent (biosorbents) as a function of the

adsorbate's concentration at a constant temperature [44]. The isotherms provide the maximum adsorption capacity for different models. The model with fitted parameters that most closely describes the data is considered as the best correlation for the experiment.

The resulting isotherm data from this study was interpreted using the Freundlich and Langmuir isotherm models. The Freundlich isotherm describes the solute concentration (arsenic) on the adsorbent surface (biosorbent) compared to the solute concentration in the liquid solution [45]. The Freundlich isotherm model assumes that there is a distribution of available surface sites where the adsorption can occur. In the context of this thesis, the Freundlich Isotherm is expressed as

$$q_e = K_f C_e^{1/n}$$

where q_e = amount of Arsenic adsorbed at equilibrium ($\mu g \cdot mg^{-1}$);

C_e = concentration of Arsenic species in aqueous phase ($\mu g. g^{-1}$);

Freundlich constants: K_f = adsorption capacity ($g \cdot mg^{-1}$);

n = intensity of adsorption.

The Langmuir isotherm model also describes the solute concentration above the adsorbent surface compared to the solute concentration in the liquid solution [46]. However, the primary difference between the Langmuir and Freundlich models is that the Langmuir model assumes mono-layer adsorption with a single surface site. For the purpose of this thesis, the Langmuir isotherm is described as:

$$q_e = Q_o b C_e / (1 + b C_e)$$

where q_e = amount of Arsenic adsorbed at equilibrium ($\mu g \cdot mg^{-1}$);

C_e = concentration of Arsenic species in aqueous phase ($\mu g. g^{-1}$);

Q_o = adsorption capacity ($\mu g \cdot mg^{-1}$);

b = energy of adsorption ($g/\mu g$).

Data from the adsorption isotherm experiments is interpreted using both the Langmuir and Freundlich isotherm models to determine the adsorption capacity of the biosorbent. Model fitting is accomplished using the error and linearity metrics defined above within the "Reaction Order Determination" section.

3.5. Desorption Experiments

Desorption describes the phenomenon of a species returning to an aqueous phase after it had previously been adsorbed. Desorption may occur due to a change in pH, temperature, a physical perturbation, or other factors. Desorption experiments were carried out in order to assess whether or not the biosorbents released any of the adsorbed arsenic back into a deionized aqueous solution [47], [48]. A total of eight experiments (outlined in Table 5) were used to assess desorption.

Table 5

Desorption experimental setup.

Arsenic Species	Buffer Conditions	Expt #	Saturated Biosorbent	Number of Reactors
As (III)	Buffered	1	Coffee Grounds	3 replicate X 8 time intervals
		2	Rice Husk	
	Non Buffered	3	Coffee Grounds	
		4	Rice Husk	
As (V)	Buffered	5	Coffee Grounds	
		6	Rice Husk	
	Non Buffered	7	Coffee Grounds	
		8	Rice Husk	

The centrifuged biosorbents from the kinetics experiments were separated out via centrifugation and recovered for the desorption experiments. An approximate loss of 10 % of the initial biosorbent mass was factored into the desorption experiment setup. The recovered biosorbents from each reactor were placed into 15 mL of clean DI water and mixed on a laboratory rotator. Samples were collected over 8 time intervals that coincided with the time intervals used to assess the kinetic experiments (including t= 0, 2, 4, 8,16,24,36 and 48 hours).

3.6. Data Interpretation

The mean and standard deviation concentration of arsenic in the aqueous phase of each time interval triplicate sample were calculated in Excel based upon individual replication concentrations determined through AAS analysis. The difference between the initial arsenic concentration and the arsenic concentration at time = t was used to determine the amount of arsenic removed from the system as a function of time.

The mass of arsenic adsorbed to the surface of the biosorbent is calculated as the difference in the arsenic mass in a reactor's aqueous phase at time = 0 hours and the concentration of arsenic in the same reactor's aqueous phase at time = t. The mass of arsenic in the reactor is calculated by multiplying the initial concentration of arsenic in the reactor by the reactor volume.

Individual replicate from each experiment were used to determine a mean and standard deviation for the reaction rate constants, percentage removal, and isotherm constants. The resulting mean and standard deviation of each parameter was then compared against the null hypothesis that the means for each parameter were the same for each biosorbent using either a single factor analysis of variance (ANOVA) or the student's t-test. ANOVA was used to compare the mean arsenic removal and the mean kinetic rate constants for all three biosorbents and if the null hypothesis was rejected a follow up multiple comparisons test was performed to tell which means were different. The t-test was used to compare the adsorption capacity between rice husk and coffee grounds. Significance of the statistical testing was evaluated at the 95% confidence interval.

4. RESULTS AND DISCUSSION

4.1. Arsenic Removal from Aqueous Samples Using Biosorbents

Three different biosorbents: coffee grounds, rice husk and coconut substrate were evaluated for their ability to remove arsenate (As V) and arsenite (As III) from buffered and non buffered solutions. The solutions had an initial arsenic concentration of 500 μg/L (ppb) and a biosorbent concentration of 1 g/l. pH was not adjusted during the course of the experiment. [49].

Figures 4 and 5 and Table 6 present the results of the kinetic experiments. Buffering was found to have no effect on arsenic adsorption onto the biosorbents. Maximum removal of As (III) occurred on coffee grounds, followed by rice husks, and then coconut substrate. After 48 hours the maximum observed removal for arsenite on coffee grounds, rice husk, and coconut substrate was 84 ± 0.28%, 68 ± 0.14%, and 26 ± 0.44%, respectively. Based upon ANOVA the null hypothesis was rejected ($p<0.05$) and a follow up t-test indicated each of the mean values were different from each other.

Comparison between the mean values of coffee grounds and rice husk resulted in 2-tailed p value <0.05. Similar comparison between coconut substrate and rice husk and coffee grounds and coconut substrate also resulted in 2-tailed p values <0.05. Therefore, based upon the constraints of our testing system, coffee grounds out performed rice husk and coconut substrate for the removal efficiency of As (III).

Removal of As (V) onto the biosorbents also followed the same trend, but exhibited higher overall removal. After 48 hours the maximum observed removal of arsenate on coffee grounds, rice husk, and coconut substrate was 91

± 1.68%, 72 ± 2.2%, and 24 ± 2.2%, respectively. Although the standard deviation values are higher than observed for As (III), it is important to point out that these deviations are less than 3% of the initial adsorbate concentration. Through ANOVA the null hypothesis was rejected ($p<0.05$) and a follow up t-test indicated each of the mean values was different from the others.

Comparison between the mean values of coffee grounds and rice husk resulted in 2-tailed p value <0.05. Similar comparison between coconut substrate and rice husk and coffee grounds and coconut substrate also resulted in 2-tailed p values <0.05. Therefore, based upon the constraints of our testing system, coffee grounds out performed rice husk and coconut substrate for the removal efficiency of As (V). Buffering did not have a statistical effect on the mean removal for As (V) and As (III) by adsorption onto the biosorbents based upon t-testing results for each biosorbent with each pair providing the significance (p value) <0.05.

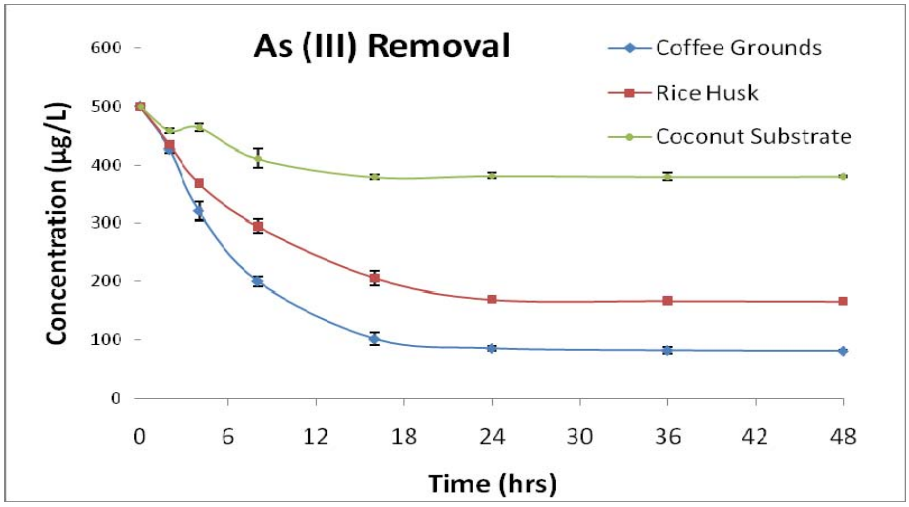


Figure 4. Concentration of As (III) in aqueous phase during adsorption kinetic experiments carried out under pH buffered conditions.

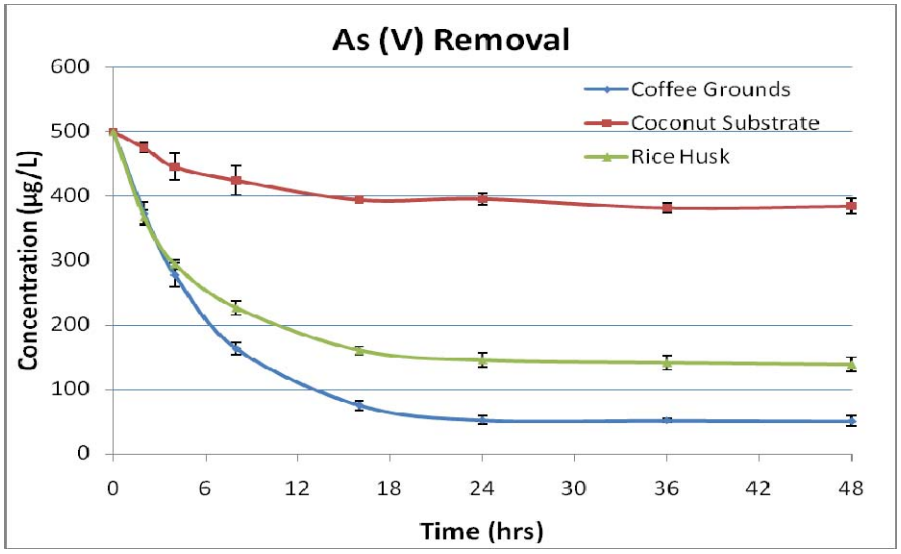


Figure 5. Concentration of As (V) in aqueous phase during adsorption kinetic experiments carried out under pH buffered conditions.

Table 6

Mean arsenic concentration (ppb) measured in triplicate reactor aqueous phase samples at 36 hours for pH buffered and non buffered conditions. The initial concentration of As (III) and As (V) were both 500 ppb (nominal). The pH of the system is also reported.

Biosorbent	As (III)					
	Buffered			Non Buffered		
	Mean (Std Dev) ppb	Mean Removal (%)	pH	Mean (Std Dev) ppb	Mean Removal (%)	pH
Coffee Grounds	**81.4 (5.2)**	**83.7**	**8.4**	**79.4 (4.9)**	**84.0**	**6.8**
Rice Husk	167 (0.6)	66.6	8.2	157 (2.1)	68.2	6.6
Coconut Substrate	380 (6.9)	24.1	8.4	368 (5.3)	25.6	6.7
Biosorbent	As(V)					
	Buffered			Non Buffered		
	Mean(Std Dev) ppb	Mean Removal (%)	pH	Mean(Std Dev) ppb	Mean Removal (%)	pH
Coffee Grounds	**51.7 (3.8)**	**89.6**	**8.2**	**44.3 (0.6)**	**91.1**	**6.7**
Rice Husk	141 (11)	71.8	8.1	144 (5.2)	71.0	6.5
Coconut Substrate	382 (7.3)	23.5	8.4	395 (7.9)	20.4	6.7

4.2. Reaction Kinetic Experiments

Figures 6 and 7 present the results of kinetic rate modeling using pseudo first order, pseudo second order and modified second order models to describe the adsorption of As (III) and As (V) onto biosorbents. The evaluation of the model fitting parameters is given in Table 7. Overall, the pseudo first order kinetic model best fits the experimental data for As (III) for all biosorbents and for As (V) on coffee grounds and coconut substrate. For the adsorption of As (V) onto rice husk, the pseudo 2nd order reaction described the experimental data provides a better fit than the pseudo 1st order model. However, the pseudo 1st order model describes As (V) adsorption on to rice husk within acceptable error (8.6%) and linearity ((0.997) and for the purposes of this discussion the pseudo 1st order model will be used.

Based upon the kinetic modeling results, the rate constants for the adsorption of arsenic onto the biosorbents following the pseudo 1st order model range from 0.13 hr^{-1} for adsorption of As (III) onto each biosorbent to 0.17 hr^{-1} for adsorption of As (V) onto rice husk and coffee grounds. ANOVA testing indicates to reject the null hypothesis ($p < 0.05$). However the amount of arsenic adsorbed to each biosorbent is different. This difference will be quantified based upon the isotherm results.

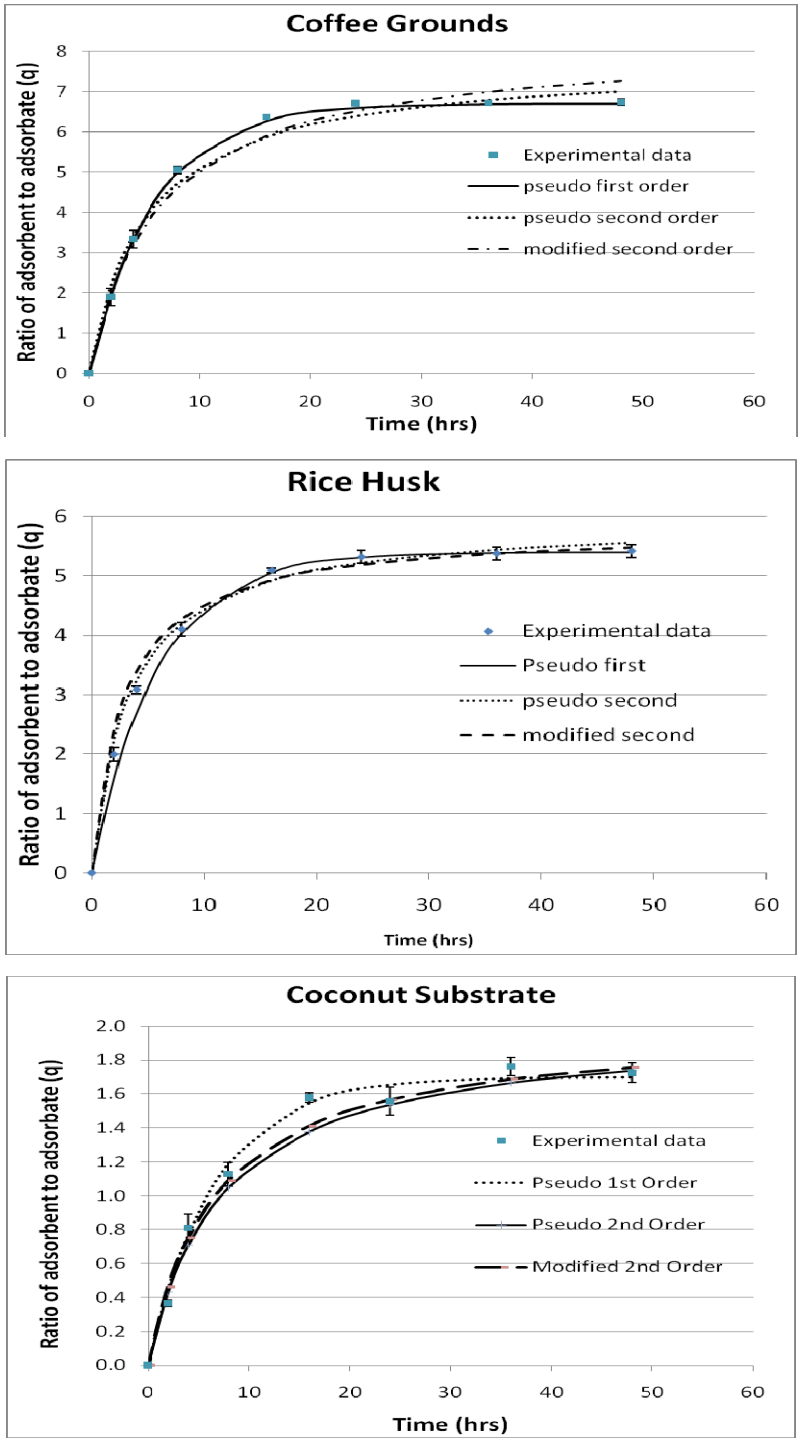


Figure 6. As (V) reaction kinetics with biosorbents in buffered conditions.

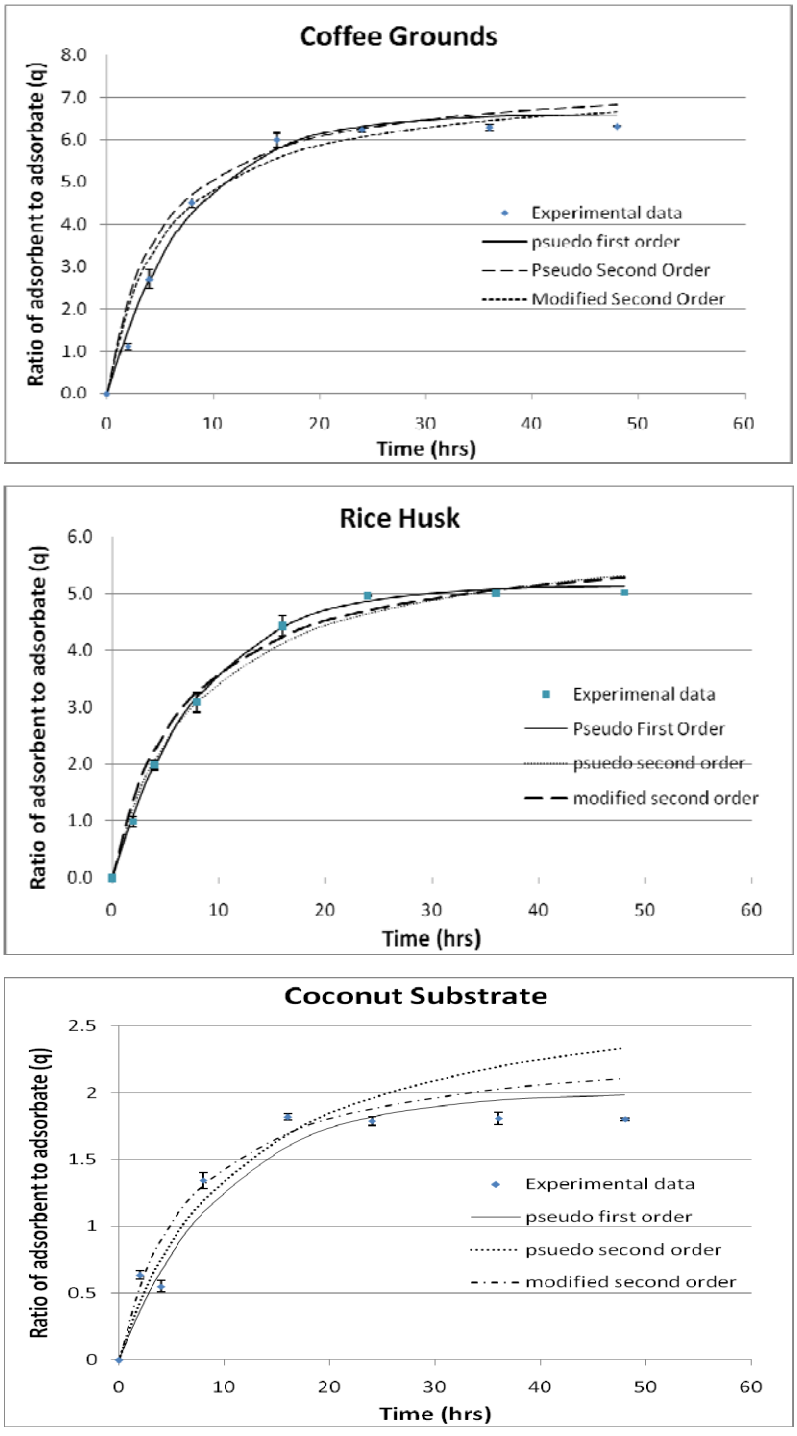


Figure 7. As (III) reaction kinetics with biosorbents in buffered conditions.

Table 7

Reaction kinetics for buffered As (III) and As (V) solutions (500 ppb) and 1 g/L biosorbent concentration. The best model fit is bolded.[1, 2]

As (III)												
	Coffee Grounds				Rice Husk				Coconut Substrate			
Biosorbent	Δ q %	r^2	k	m_e	Δ q %	r^2	k	m_e	Δ q %	r^2	k	m_e
Pseudo 1st order	**12.9**	**0.99**	**0.13**	**6.6**	**4.13**	**0.99**	**0.13**	**5.2**	**18.9**	**0.91**	**0.13**	**0.2**
Pseudo 2nd order	36.4	0.97	0.03	7.5	9.45	0.98	0.02	6.2	22.3	0.87	0.13	2.9
Modified 2nd order	30.2	0.98	0.19	7.4	15.2	0.99	0.15	6.0	24.3	0.89	0.12	0.5
As (V)												
	Coffee Grounds				Rice Husk				Coconut Substrate			
Biosorbent	Δ q %	r^2	k	m_e	Δ q %	r^2	k	m_e	Δ q %	r^2	k	m_e
Pseudo 1st order	**1.28**	**0.99**	**0.17**	**6.7**	8.91	0.99	0.17	5.4	**8.16**	**0.98**	**0.15**	**1.7**
Pseudo 2nd order	6.56	0.98	0.02	7.7	**4.83**	**0.99**	**0.05**	**5.9**	9.49	0.97	0.069	2
Modified 2nd order	8.18	0.99	0.16	8.2	8.18	0.99	0.35	5.8	10.4	0.97	0.15	2

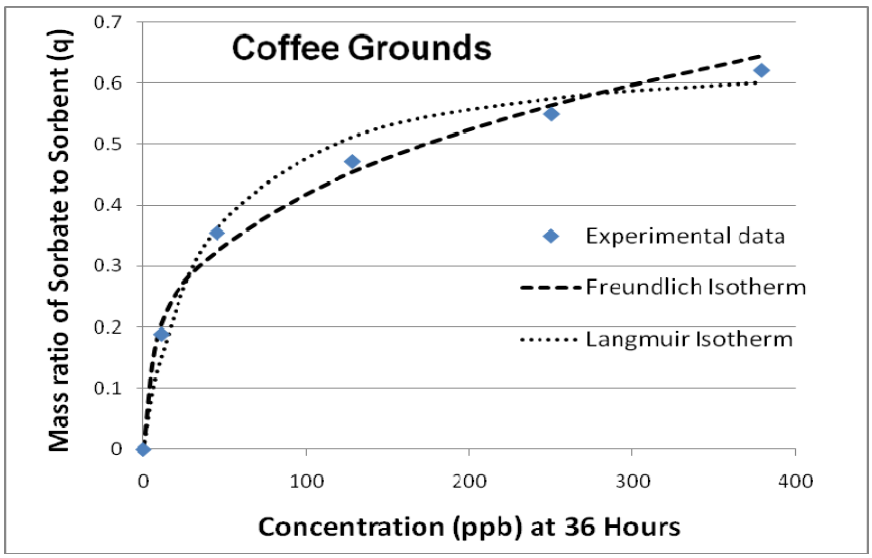
[1] model equations: pseudo 1st order: $m_t = m_e[1 - exp(- k_1 t)]$, pseudo 2nd order: $m_t = t / (1/k_2 m_e^2) + (t/m_e)$, modified 2nd order: $m_t = m_e(1 - [1 / \beta + k_2 t])$

[2] m_e = amount of arsenic adsorbed at equilibrium (μg); m_t = amount of arsenic adsorbed at any time (μg); t = reaction duration (hours); k_1 and k_2 are the first- and second-order rate constants (hr-1); β is an initial biosorbent loading describing constant = 1; r^2 = correlation coefficient; Δq (%) = $100 \cdot ((\Sigma[(m_{t,experimental} - m_{t,modeled})/m_{t,experimental}]^2)/(n - 1))^{1/2}$ where n = number of data points.

4.3. Isotherm Experiments

Figures 8 and 9 present the results of the isotherm experiments for the adsorption of As (III) and As (V) onto coffee grounds and rice husk under pH buffered conditions. The coconut substrate was not assessed because this biosorbent's overall removal was much lower than observed for the other two sorbents. The adsorption capacity of rice husk and coffee grounds was estimated by fitting the experimental data to the Freundlich and Langmuir isotherm models. The results from the isotherm models are summarized in Table 8. In each case the Freundlich model does a better job of describing the data, indicating that the surface has a distribution of binding sites. However, because the Freundlich model allows for a theoretically infinite adsorption capacity, the Langmuir model (which also describes the experimental data $r^2 > 0.95$ and $\Delta q < 37\%$ for worst fit) was used to determine the maximum adsorption capacity for As (III) and As (V) for both coffee grounds and rice husk.

Based upon the Langmuir model estimate, the maximum adsorption capacities (q_m) for As (III) and As (V) on coffee grounds was found to be 0.66 and 0.70 mg/g, respectively. For rice husk, the q_m for As (III) and As (V) was found to be 0.55 and 0.66 mg/g, respectively. Statistical evaluation comparing the mean adsorption capacities for As (III) and As (V) on coffee grounds versus rice husk using a two sided t-test assuming equal variance indicates that the null hypothesis can be rejected for As(V) ($p = 0.0015$), but not for As(III) ($p = 0.108$). Therefore, it is concluded that coffee grounds have a higher adsorption capacity for As (V) than rice husk but have a comparable adsorption capacity for As (III).



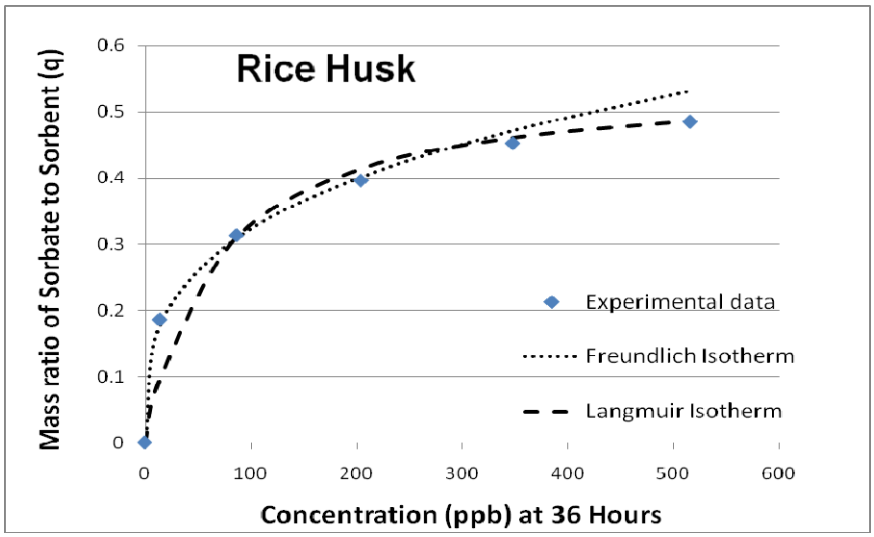


Figure 8. As (III) Isotherm models with biosorbents in buffered conditions.

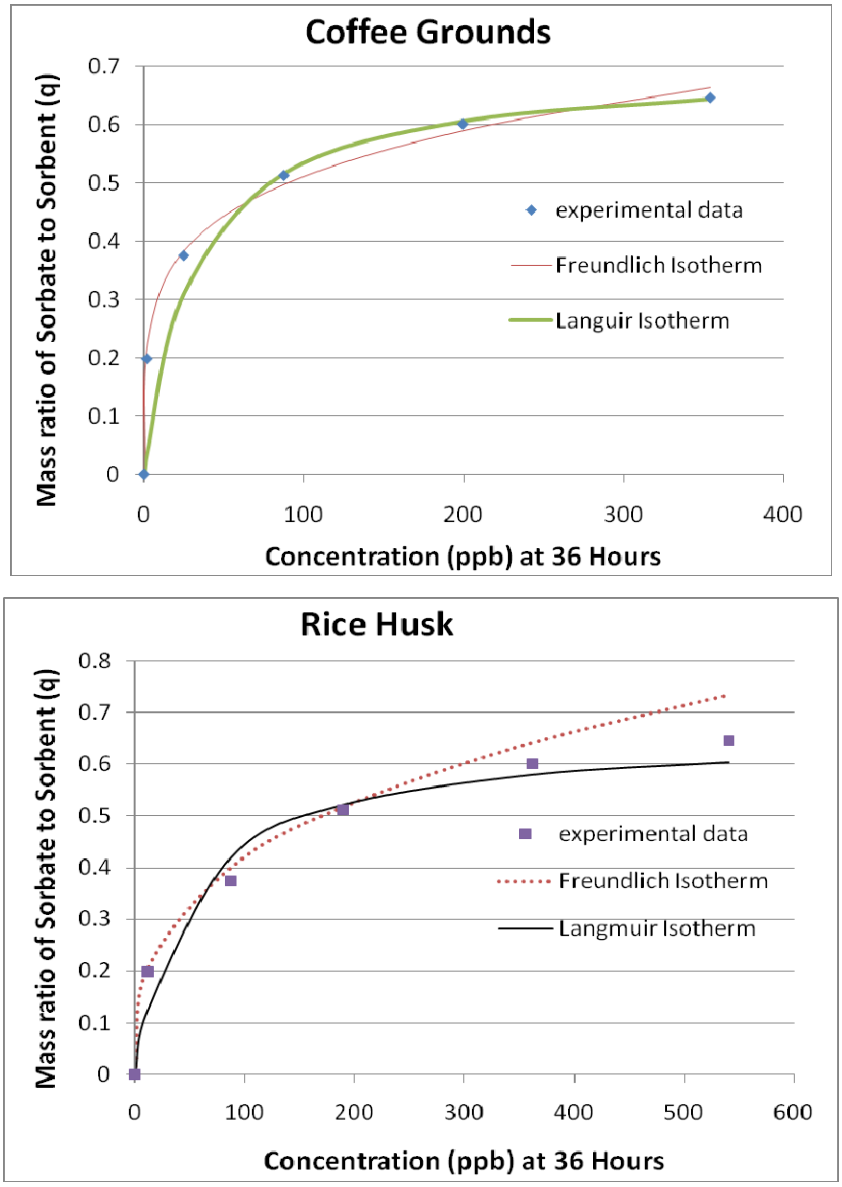


Figure 9. As (V) Isotherm models with biosorbents in buffered conditions.

Table 8

Coffee grounds and rice husk isotherm model parameters for buffered aqueous system[1,2,3].

Coffee Grounds							
As (III)				As (V)			
Freundlich		Langmuir		Freundlich		Langmuir	
K_f	0.10	Q_o	0.66	K_f	0.20	Q_o	0.70
N	3.10	b	0.03	n	4.85	B	0.03
r^2	0.992	r^2	0.988	r^2	0.996	r^2	0.954
Δq(%)	6.23	Δq(%)	9.89	Δq(%)	6.49	Δq(%)	36.66
Rice Husk							
As (III)				As (V)			
Freundlich		Langmuir		Freundlich		Langmuir	
K_f	0.08	Q_o	0.55	K_f	0.09	Q_o	0.66
n	3.30	b	0.02	n	3.00	B	0.02
r^2	0.994	r^2	0.968	r^2	0.993	r^2	0.973
Δq(%)	2.64	Δq(%)	21.58	Δq(%)	7.46	Δq(%)	18.09

[1] Freundlich Model Equation: $q_e = K_f C_e^{1/n}$

[2] Langmuir Single Site Model Equation: $q_e = Q_o b C_e / (1 + bC_e)$

[3] q_e *= amount of Arsenic adsorbed at equilibrium (μg · mg⁻¹);* C_e *= concentration of Arsenic species in aqueous phase (μg. g⁻¹). Langmuir constants:* Q_o *= adsorption capacity (μg · mg⁻¹), b = energy of adsorption (g/μg). Freundlich constants:* K_f *= adsorption capacity (g · mg⁻¹), n = intensity of adsorption.* r^2 *=correlation coefficient;* $\Delta q\ (\%) = 100 \cdot ((\Sigma\ [(q_{experimental} - q_{modeled})/q_{experimental}]^2)/(n - 1))^{1/2}$ *where n = number of data points; t = reaction duration (hours).*

The observed adsorption capacities determine for rice husk and coffee grounds are compared to adsorption capacities of other adsorbents reported in the literature in Table 9. While the performance of the two biosorbents to remove As (III) and As (V) are lower than activated carbon or chelating resins, the estimated adsorption capacity of the two evaluated biosorbents are higher or comparable to the other reported adsorbents.

Table 9

Arsenic removal and its adsorption capacity for various adsorbents.

Adsorbent	Arsenic Species, maximum adsorption Capacity, q_m (mg/g)		Reference
	As (III)	As (V)	
Iron Oxide Uncoated Sand	0.006		[1]
Activated Carbon	29.9	30.48	[1]
$Al_2O_3/Fe(OH)_3$		0.09	[1]
Activated Alumina	0.18		[1]
Amorphous Iron Hydroxide		7	[50]
Human Hairs		0.012	[1]
Iron (III) loaded Chelating Resin		60	[1]
Titanium Pillared Clay		3	[50]
Rice Husk	0.55	0.66	this study
Coffee Grounds	0.66	0.7	this study
Rice Husk (Total As)	1.22		[51]
PineWood Char		0.012	[1]
Windsor Soil		0.55	[1]

A higher adsorption capacity for arsenic removal on rice husk was reported by Kalderis *et al*. [39] with an adsorption capacity of 1.22 mg/g for total arsenic from water. A better understanding of the relationship betweent the Kalderis study and our study results could be achieved if the surface area of the rice husk biosorbents were given. It would also be useful to know if chaff was separated from the rice husk used in the Kalderis experiment. As surface area has a positive effect on enhancing an adsorbent's ability to remove an adsorbate, normalizing the adsorption capacity results for surface area when comparing between the same adsorbents in different studies and between different sorbents in the same studies is of future interest.

4.4. Desorption

Results of the desorption experiment are presented in Figure 10. Desorption of both As (III) and As (V) occured from the biosorbents when they were placed into clean water. The observed rate of desorption reaches a constant value after 20 hours. Desorption was observed in both pH bufered and non buffered aqueous systems.

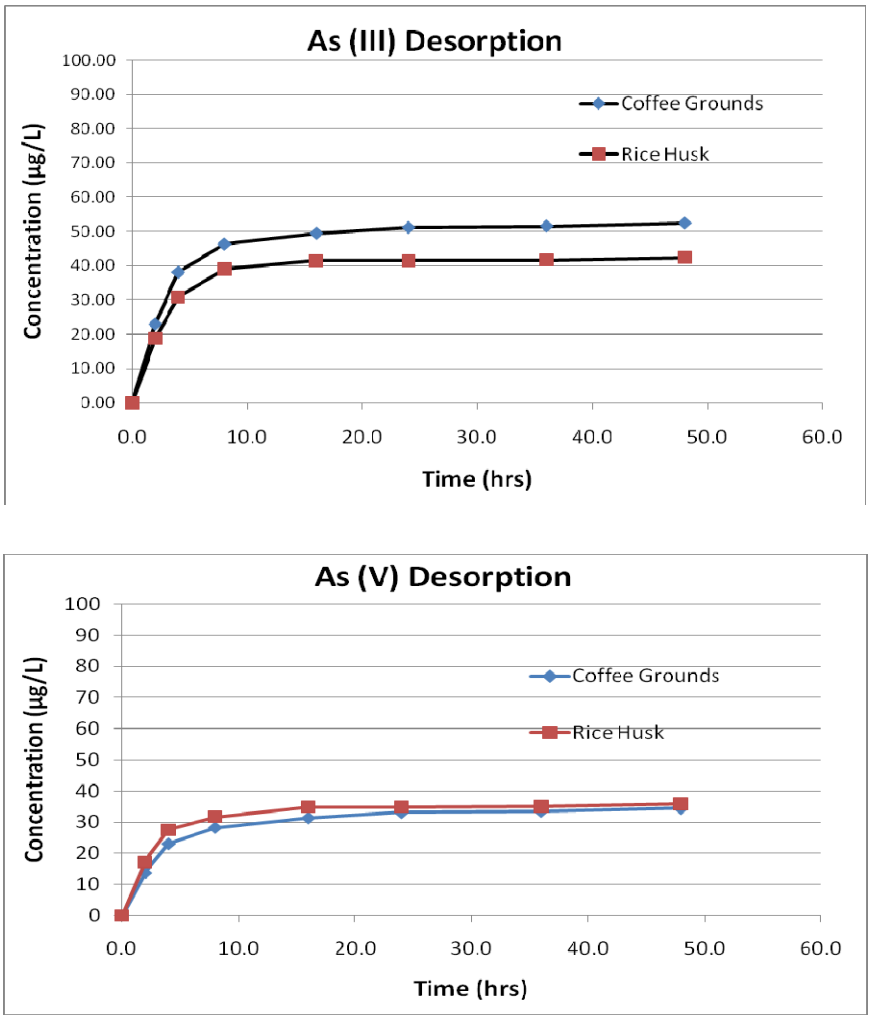


Figure 10. Desorption graphs for coffee grounds and rice husk under pH buffered conditions for As (III) and As (V).

For coffee grounds, approximately 12% and 8% of the overall adsorbed mass desorbs back into solution with As (III) and As (V) respectively over 48 hours. The corresponding desorption removal percentages for rice husk were 12.5% and 10% respectively. Statistical evaluation comparing the mean desorption percentages for As (III) and As (V) on coffee grounds versus rice husk using a two sided t-test assuming equal variance indicates that the null hypothesis cannot be rejected for As(III) ($p = 0.7921$) and As(V) ($p = 0.5259$). Therefore, based upon the magnitude of desorption and the statistical comparisons of the means, it is concluded that coffee grounds and rice husks have comparable desorption for As (III) and As (V). These results indicate that the biosorbents have the tendency to desorb to a limited extent and the phenomenon of desorption needs to be considered while developing applications of the biosorbent adsorption technology.

5. SUMMARY

Rice husk, coffee grounds and coconut substrate were successfully evaluated for their ability to remove As (III) and As (V) from pH buffered and non-buffered water at initial arsenic concentrations of 500 ppb. Mean removal of As (III) observed on each biosorbent were not statistically similar at the 95% confidence interval for any of the sorbents. Therefore, based upon the test system conditions the performance of the three biosorbents to remove As (III) was best for coffee grounds (>80%), followed by rice husk (>65%), and the coconut substrate (<30%) under both pH buffered and non buffered conditions.

Interestingly, the reaction rate of the adsorption of arsenic was statistically similar for all three adsorbents. However, the total amount of arsenic adsorbed was different. This finding indicates that the adsorption is not limited by the kinetics of the reaction, but rather limited by the diffusion within the adsorbent. The initial pseudo 1^{st} order reaction rate constant observed for As (III) was about 0.13 hr^{-1} for all the biosorbents and for As (V) was 0.17 hr^{-1} in the case of coffee grounds and rice husk and 0.15 hr^{-1} for coconut substrate.The adsorption capacity of coffee grounds and rice husks was explored using adsorption isotherms and the results were fit to both the Freundlich and Langmuir isotherm models. While the Freundlich model described the data with higher linearity and lower better standard error, the Langmuir model was used to determine the maximum adsorption capacity for both adsorbents.

The maximum adsorption capacity of coffee grounds for removal of As (III) and As (V) were 0.66 and 0.70 mg/g, respectively. Similarly, the maximum adsorption capacity for the removal of As (III) and As (V) onto rice husk was determined to be 0.55 and 0.66 mg/g, respectively. While the mean adsorption capacity for As (III) was statistically similar for both biosorbents, the mean adsorption capacity for As (V) was not statistically similar for both biosorbents. As a result, the adsorption capacity of As (V) is higher for coffee grounds, but the adsorption capacity of As (III) is comparable for both biosorbents. While the experiments that were performed as part of this thesis suggest that coffee grounds can remove both arsenic from water better or equivalent to rice husk, desorption needs to be considered in developing applications of this biosorbent technology since desorption of both As(III) and As(V) (<15% of sorbed mass) was observed. Overall, however, the results of this thesis work reveal that coffee can be used as an effective biosorbent when compared to rice husk; however, coconut substrate is less effective at removing As (III) and As (V).

6. FUTURE SCOPE

The experiments conducted as part of this thesis indicate the potential of these biosorbents to remove arsenic under laboratory conditions. However, the impact of different system conditions such as effect of temperature, pH, and presence of other metals (such as copper, mercury, or zinc as examples) needs to be further characterized. Additional analytical techniques such as Inductively Coupled Plasma Mass Spectrometry (ICPMS) and X-ray Photoelectron Spectroscopy (XPS) will help clarify the surface structure of these biosorbents. Additional surface modification of the biosorbent (such as acid washing, grinding, or charring as examples) can also be important factors affecting removal performance and needs to be further characterized. Each of these remaining issues should be addressed as part of future work.

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